REDUCTION KINETICS OF IRON ORE PELLETS AND THE EFFECT OF BINDERS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

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In

Metallurgical and Materials Engineering

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CERTIFICATE

This is to certify that the thesis entitled , " Reduction Kinetics of Iron Ore Pellets and the Effect of Binders" submitted by Ms Itishree Mishra & Ms Asima Priyadarsini in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Metallurgical and Materials Engineering at the National Institute of Technology , Rourkela (Deemed University) is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge , the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

Abstract

Reduction of Iron Ore Pellets was carried out for the temperature range 900 to 1100°C. In reduction kinetic study the most satisfactory model was to take the slope of the initial linear region of fractional reduction vs. time curve as a measure of rate constant (k). In k vs. 1/T plots were straight line from which Activation Energy was calculated. Pellets having different percentages of binders were reduced and compared to find the effect of binders.

Introduction

Iron ore in a finely ground state is not easily transported or readily processed .Thus it is necessary to agglomerate the fine ground ore into pellet using binders. Inorganic binders introduce silica which decreases the final ore content of the pellet. Hence organic binders were developed. Use of pellets increases the productivity in blast furnace and reduces coke consumption.

Experimental

Iron ore from M.G.Mohanty mines and charcoal were used in the experiment .Analysis of the iron ore showed that it contained 63.7%Fe, 1.6%SiO_2, and 1.4% Al_2O_3. The reaction carried out in the experiment is mainly of direct reduction because here we have used charcoal. The iron ore was crushed , ground and screened to 100# size and charcoal to 72# size. Pellets were made by hand rolling method by using water and different quantities of binder. The pellets were fired at different firing temperature. Each crucible containing iron ore pellets were placed in a furnace and reduction was carried out at different temperature from 900-1100°C with time intervals of 5,10, 15……… minutes. Six crucibles containing pellets of different % binder(0.5%,1%,2%)were taken & reduction was carried out at a constant temperature of 950°C and pellets were taken out at a time interval of 10,20,30,40,50,and 60 minutes. The product obtained after reduction was then taken for the study and analysis of reduction behaviour.

Analysis

Percentage reduction is found as

$$R = \frac{\text{Initial oxygen content} - \text{Final oxygen content}}{\text{Total oxygen content initially}} \times 100\%$$

With the help of the Arrhenius equation $\mathbf{K = A\, e^{-E/RT}}$, we can calculate the activation energy.

Where, K = Rate Constant, A= Arrehenius Constant,

E= Activation Energy, R= Gas Constant, T= Temperature.

We plotted the graph of ln (K) vs. ($1/T \times 10^4$) for pellets with binder, with bentonite and with dextrin. Slope of this graph x (universal gas constant) = activation energy (E)

Results

- With increase in temperature, the percentage reduction increases with increase in time.
- The percentage reduction in case of pellet with Dextrin was found more. This may be because of the lower activation energy of the pellets with dextrin as a binder.
- A number of Models were considered out of which the model $1-(1-R)^{1/3}=kT$ exactly fits to our experimental values.
- Lower the binder percentage, greater the reducibility (.5% >1%>2%). This is due to a decrease in the porosity with increasing binder percentage.
- The activation energy of a pellet with **0.5% bentonite** binder is **Ea= 20.701 Kcal/mole** and the activation energy for pellet with dextrin binder is **Ea=17.423 Kcal/mole.** So the rate of reaction in case of pellets with Dextrin is faster than the rate of reaction of pellets with Bentonite.

Conclusions

1. Topochemical reaction phenomenon was observed.
2. With the increase of time, percentage reduction (O_2 removal) increases in all the pellet samples.
3. With the increase of temperature, percentage reduction increases up to a certain extent.
4. Almost a mixed controlled reaction was obtained as the activation energy is in between 10 kcals/mole and 30 kcals/mole.
5. Reduction reaction is temperature dependant.
6. Lower the binder percentage, greater the reducibility (.5% >1%>2%).

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Chapter 1

INTRODUCTION

Background

Objectives

Introduction

Blast Furnace is used mainly for pig iron production all over the world. Thus because it has very high production rate and also greater degree of heat utilization to a remarkable extent as here counter current heat exchange principle is utilized.

With time the use of pellets as raw material for blast furnace has increased considerably. As blast furnace feed, it offers much scope for improving productivity and economy of coke consumption. By using pre reduced pellets an increase in production of at least 25-30% can be obtained in the existing blast furnace. In Electric Arc Furnaces pre reduced pellets have proved an adequate substitute for steel scrap.

Upgrading naturally found iron ores is accomplished by grinding the ore into fine particles so that the iron containing materials can be liberated from unwanted gangue. This beneficiation process leaves the iron ore in a finely ground state that is not easily transported or readily processed in steel making facilities. Therefore, it is necessary to agglomerate the fine ground material into pellets using various binders, afterwards indurating the newly formed pellets to strengths high enough to survive transportation.

Few examples of iron making industry by use of pellets are ESSAR STEELS, JINDAL STEELS, etc.

Following are the aims and objectives of our Project:

- To characterize the reduction behaviour of iron ore by charcoal.
- To study the effect of addition of different binders on reduction behaviour of iron ore pellets.

Chapter 2

PELLETS

Advantages

Disadvantages

Raw materials for Pelletisation

Organic & Inorganic Binders

Criteria of Binders for Pelletisation

Role of Binders

Bonding Mechanism

Pellets

Pellets are approximately spherical lumps formed by agglomeration of the crushed iron ore fines in presence of moisture and binder, on subsequent induration at 1300°C

Advantages of Pellets:

- Good Reducibility: Due to high porosity
- Good bed Permeability: Due to Spherical shape and open pores
- High Strength (150-250 kg/cm2) or More
- High Porosity (25-30%)
- Less heat consumption than sintering
- Uniform chemical composition
- Easy handling and transportation
- Good resistance to disintegration during charging
- Resistance to weathering and freezing

Disadvantages of Pellets:

- High cost of production due to grinding and firing especially with oil burners;
- Swelling and loss of strength inside of furnace;
- Sticking during firing;
- Resistance to flow of gas more than that in sinter for the same size range due to lower voidage;
- Difficulty of producing fluxed pellets;
- Fluxed pellets break down under reducing conditions much more than acid and basic sinters and acid pellets;
- Stronger highly fluxed sinters, especially containing MgO, are being increasingly preferred to pellets.

Binders are broadly classified into following categories:

- **Organic Binders:** Dextrin, Thermosetting Resin, Processed or natural oils, Peridur, Carbocel, carboxymethyl cellulose
- **Inorganic Binders:** Bentonite, Cement, Lime, Olivine, etc

Criteria of binders for iron ore pelletization

1) **Mechanical properties** . It should maintain good mechanical properties of green, dry, and fired pellets, e.g., deformation under load, resistance to fracture by impact and compression, resistance to abrasion.
2) **Chemical composition** . It should bring no environmentally and metallurgically harmful elements such as P, S, As, etc., into product pellets. It should not markedly reduce iron grade and increase impurities such as silica.
3) **Metallurgical performance.** It should maintain pellet's excellent metallurgical properties, e.g. reducibility, swelling during reduction.
4) **Processing behavior.** Adding, mixing, dispersion of binder, green ball preparation, pellet drying, etc., should not be too complicated or essentially change conventional pellet production method
5) **Cost factor**. Price should be acceptable for iron pellets production.

Role of Binders: Binders play an important role in pellet formation. They give strong, wet and dry balls in green state and increase fire strength.

Bonding Mechanism:

Bonding Mechanism includes two stages viz.

1. Ball Formation – Surface tension of water & gravitational force creates pressure on particles, so they coalesce together & form nuclei which grow in size into ball.

2. Induration (Heat Hardening) – Solid state diffusion at particle surfaces at higher temperature cause recrystallisation & growth giving strength.

Chapter 3

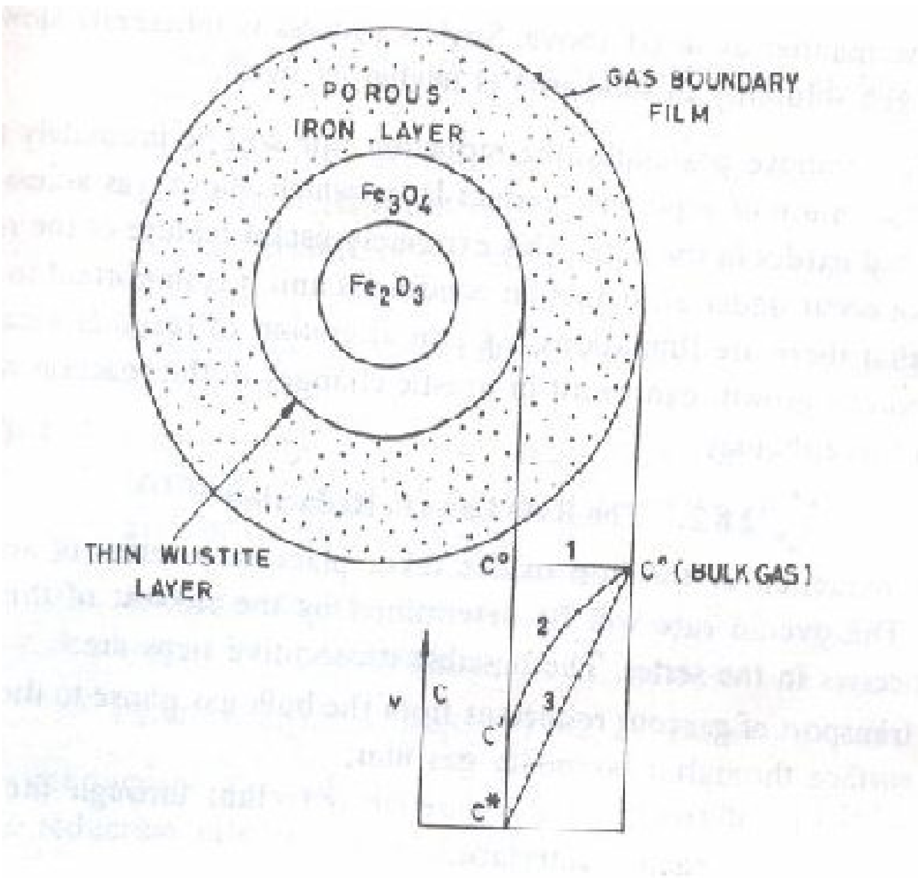
REDUCTION BEHAVIOUR

Rate Laws in Reduction

Reduction Reactions

Mechanism

Reduction kinetics of iron ore reduction deals with the rate at which iron oxide is converted to metallic iron by removal of oxygen. This influences production rate of the process, which ultimately determines the economic feasibility and competitiveness of the technologies involved.



A schematic diagram of the mode of gaseous reduction of a spherical sample of ferric oxide.possible concentration gradients of the reducing gas across the iron layer are also shown.

Figure No-1

A shell or layer of metallic iron in contact with a layer of wustite will be formed as shown in the figure. Such a structure is typical of topochemical reactions where the reacting interface between the solid reactants and the solid products move parallel to the original solid surface.

The Rate Laws in Reduction:

The reduction of the iron oxides takes place in a series of sequential steps. The overall rate will be determined by the slowest of the process or processes in the series. The possible consecutive steps are:

i. Transport of gaseous reductant from the bulk gas phase to the particle surface through a boundary gas film;
ii. Molecular diffusion of the gaseous reductant through the product layer to the reaction interface ;
iii. Adsorption of the gaseous reductant at the interface;
iv. Reaction at the interface(reaction between adsorbed reductant and oxygen of the lattice);
v. Desorption of the gaseous products from the interface;
vi. Mass transport of iron and oxygen ions and transformations in the solid phase; formation and growth of the reaction products, viz. , magnetite, wustite and iron;
vii. Molecular diffusion of gaseous products through the product layer to the particle surface;
viii. Transport of the gaseous products from the particle surface through the boundary gas film to the bulk gas phase.

The rate limiting cases are chemical control(steps iii to vi) and diffusion control (steps I & viii ; ii ; vi & vii)

Reduction Reactions

Indirect Reduction

- $\mathbf{3Fe_2O_3 + CO/H_2 = 2Fe_3O_4 + CO_2/H_2O}$
- $\mathbf{Fe_3O_4 + CO/H_2 = 3FeO + CO_2/H_2O}$
- $\mathbf{FeO + CO/H_2 = Fe + CO_2/H_2O}$

Direct Reduction

- $\mathbf{3Fe_2O_3 + C = 2Fe_3O_4 + CO}$
- $\mathbf{Fe_3O_4 + C = 3FeO + CO}$
- $\mathbf{FeO + C = Fe + CO}$
- $\mathbf{3Fe + C = Fe_3C}$
- $\mathbf{C + CO_2 = 2CO}$

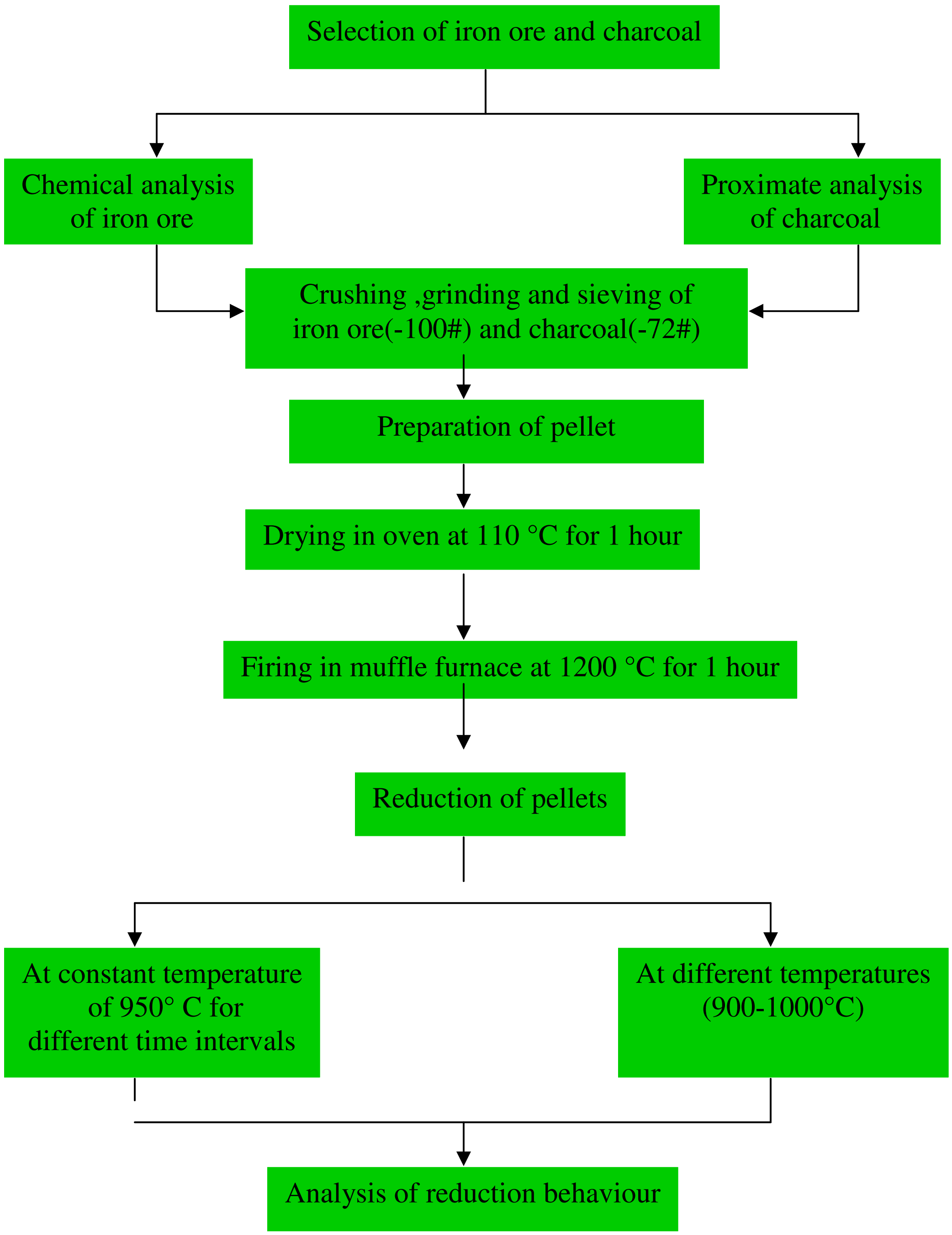
EXPERIMENTAL PROCEDURE

- M. G. Mohanty Iron ore and charcoal was taken.
- Chemical analysis of iron ore & charcoal was done
- Grinding of the ore to -100# size.
- Crushing of the charcoal to -72# size.
- Making of pellets by hand rolling using different types and quantities of of binder (0.5 to 2%) along with water.
- Air drying of pellets followed by oven drying at 110 °C to remove moisture.
- To obtain proper strength in the pellet by heat hardening i.e. by recrystallisation or gangue particles fusing to form slag phase, Firing was done in a muffle furnace at 1300°C.
- The pellet that is formed is taken inside a metallic crucible. Then the pellet is surrounded by charcoal and then reduced.
- 1st case-Each crucible containing iron ore pellets were placed in a furnace and reduction was carried out with charcoal at different temperature from 900-1100°C
- 2nd case-6 crucibles containing pellets of different % binder(.5%,1%,2%)were taken & reduction was carried out at a constant temperature of 950°C and pellets were taken out at a time interval of 10,20,30,40,50,and 60 minutes.
- Then initial weight of the iron oxide pellet and the final weight of the iron oxide pellet is measured and the percentage reduction is calculated. In both the cases, from the loss in weight plot was made between % reduction and time. Then a straight line plot between $1-(1-R)^{1/3}$ vs time was drawn. The slope of the graph gives K (rate constant).
- Then graphs were drawn for ln (K) vs $1/T \times 10^4$. Slope of the graph gives the value of activation energy which was calculated from Arrehenius Equation: $K=Ae^{-E/RT}$.

Percentage reduction can be calculated as

$$R = \frac{\text{Initial oxygen content} - \text{Final oxygen content}}{\text{Total oxygen content initially}} \times 100\%$$

FLOWSHEET


Selection of iron ore and charcoal
Chemical analysis of iron ore
Proximate analysis of charcoal
Crushing ,grinding and sieving of iron ore(-100#) and charcoal(-72#)
Preparation of pellet
Drying in oven at 110 °C for 1 hour
Firing in muffle furnace at 1200 °C for 1 hour
Reduction of pellets
At constant temperature of 950° C for different time intervals
At different temperatures (900-1000°C)
Analysis of reduction behaviour

OBSERVATIONS:

Table No-1: Charcoal Proximate Analysis Results

% Moisture	8.66%
% Volatile Matter	9.33%
%Fixed Carbon	73.65%
% Ash	8.36%

Table No-2: Iron ore Chemical Analysis Results

Fe	63.7%
MnO	0.07%
SiO_2	1.6%
Al_2O_3	1.4%

GRAPHICAL ANALYSIS:

The graphical analysis was done by plotting a graph of **reduction vs. time** and the effect of different binders on reduction time will be studied.

Reducibility of pellets decreases with the increase of binder. This is due to a decrease in the porosity.

Table No-3: Percentage Reduction versus time for Pellet with Dextrine

Time(in minutes)	0.5% Dextrine (in %)	1%Dextrine (in %)	2%Dextrine (in %)
10	27.3	19.2	16.7
20	46.8	39.7	32.5
30	65.1	58.2	53.4
40	84.5	77.2	69.8
50	92.6	85.9	79.8
60	93.0	87.1	80.7

Figure No 2- Percentage Reduction versus time for Pellet with Dextrine

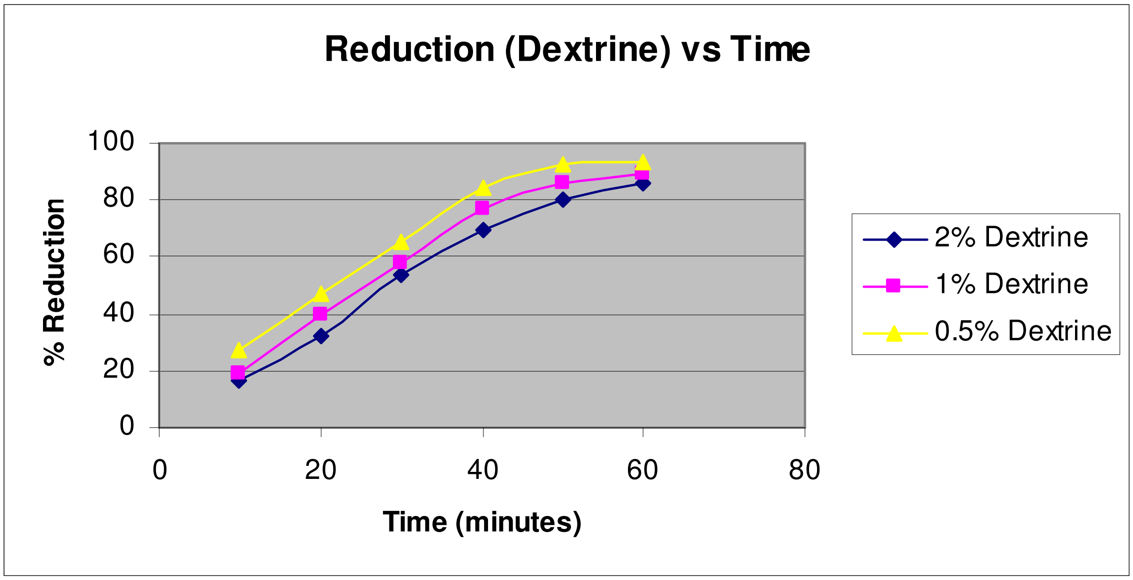


Table No-4: Percentage Reduction versus time for Pellet with Bentonite

Time(in minutes)	0.5% Bentonite (in %)	1% Bentonite (in %)	2% Bentonite (in %)
10	18.6	15.3	10.9
20	35.4	29.6	25.1
30	54.2	46	41.2
40	76	67.5	61.3
50	89.7	80.4	75.6
60	92.8	86.8	80.2

Figure No 3: Percentage Reduction versus time for Pellet with Bentonite

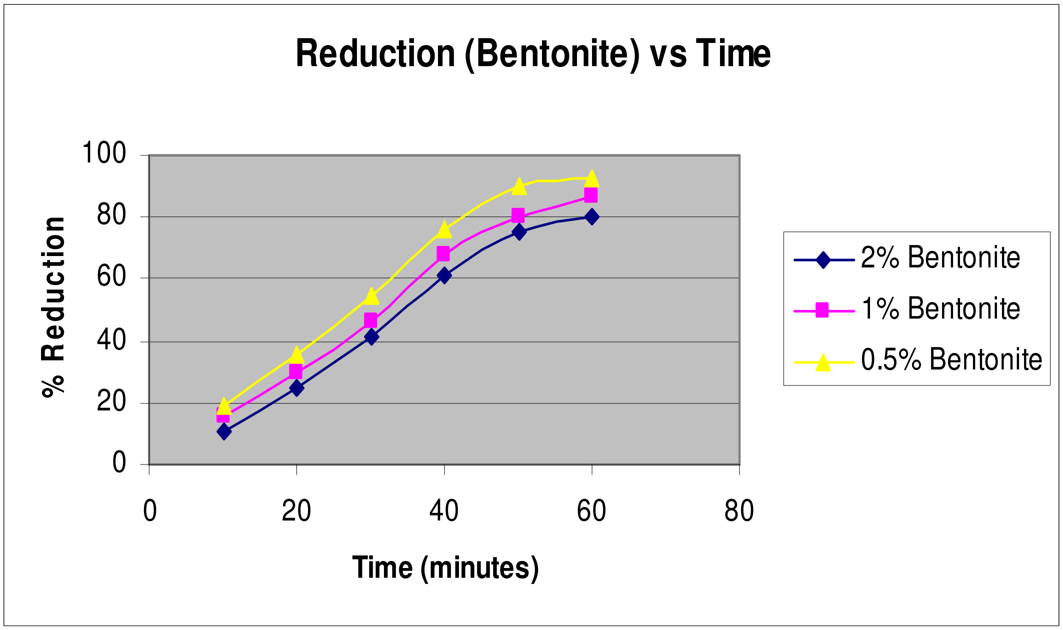


Figure No. 4:-Comparision of reduction of pellets with 0.5% binder with bentonite and dextrine

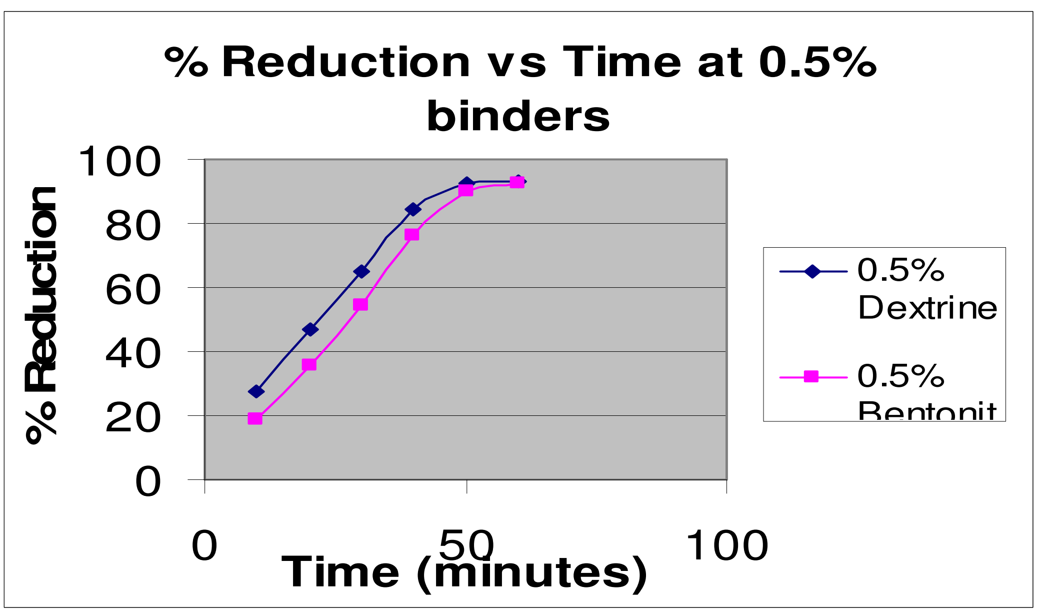


Figure No .5:-Comparision of reduction of pellets with 1 % binder with bentonite and dextrine

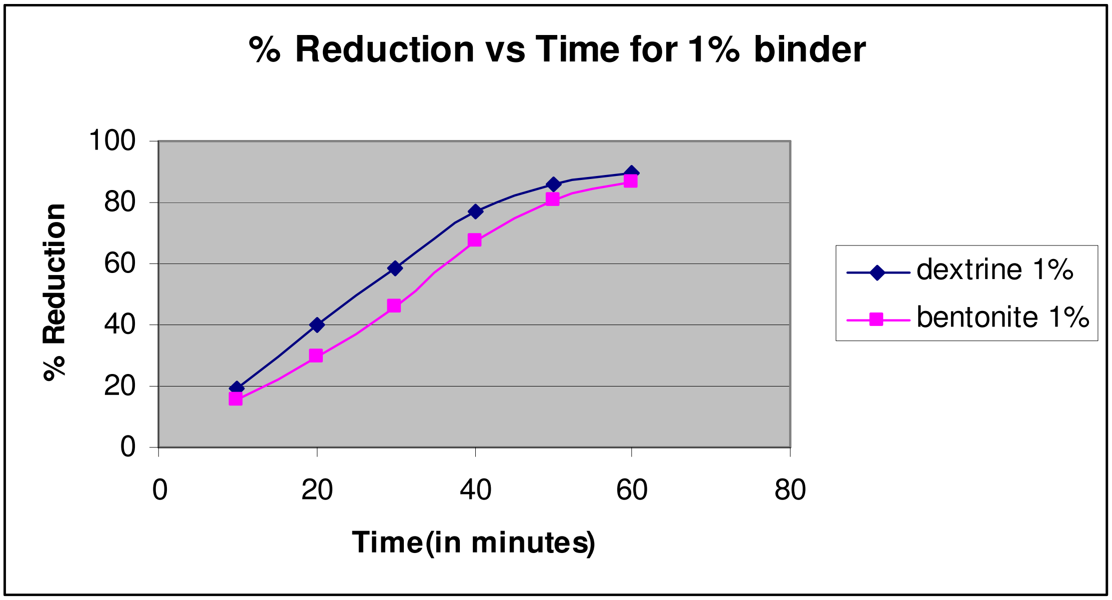
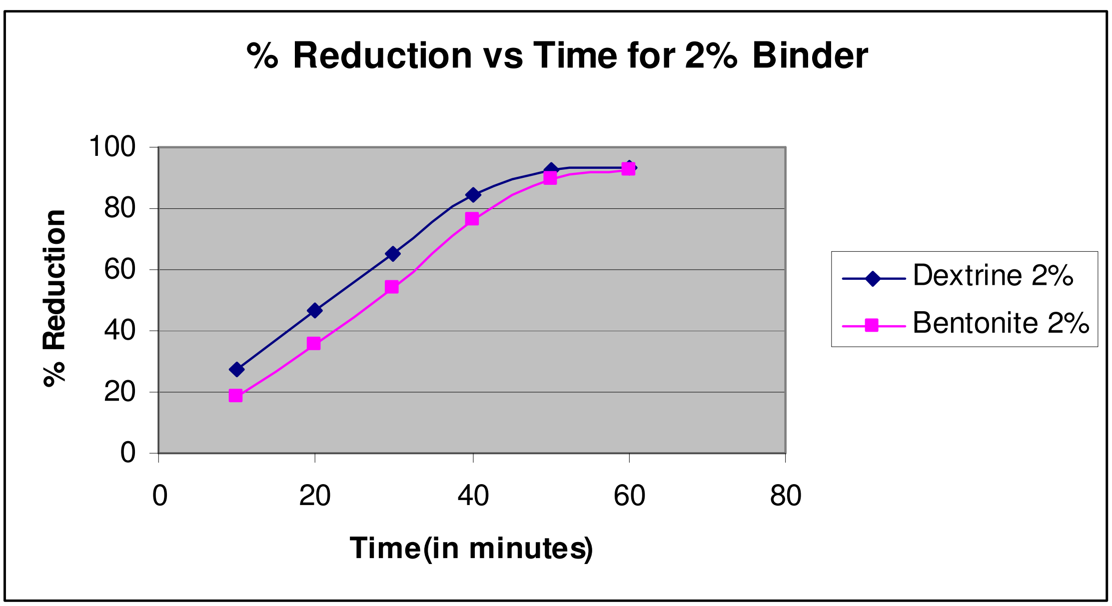


Figure No.6:-Comparison of reduction of pellets with 2 % binder with bentonite and dextrine



1-(1-R) $^{1/3}$ versus Time (minutes)

A number of Models were considered but the model 1-(1-R) $^{1/3}$= KT exactly suits our experimental values and gives us a straight line, so that we can evaluate the value of K.

Table No. 5 : 1-(1-R)$^{1/3}$ versus Time for Pellets with Dextrine

Time (in minutes)	0.5% dextrine	1% dextrine	2% dextrine
10	0.1008	0.0686	0.0591
20	0.1897	0.1552	0.1228
30	0.2959	0.2523	0.2247
40	0.4628	0.3891	0.3291
50	0.5802	0.4795	0.4133

Figure No 7: 1-(1-R) $^{1/3}$ versus Time for Pellets with Dextrine

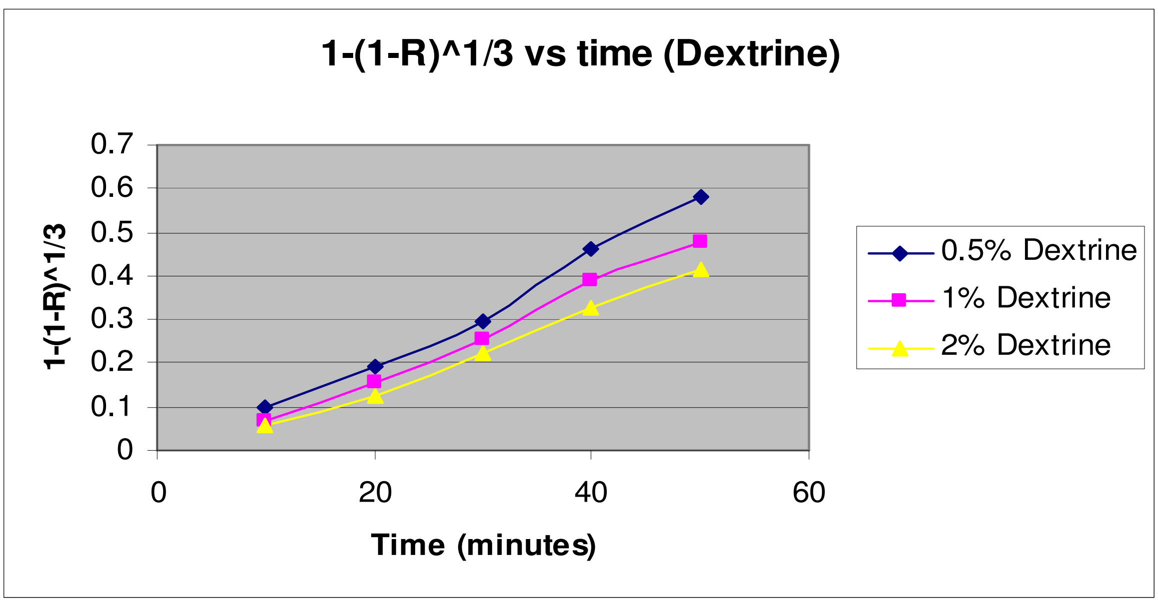
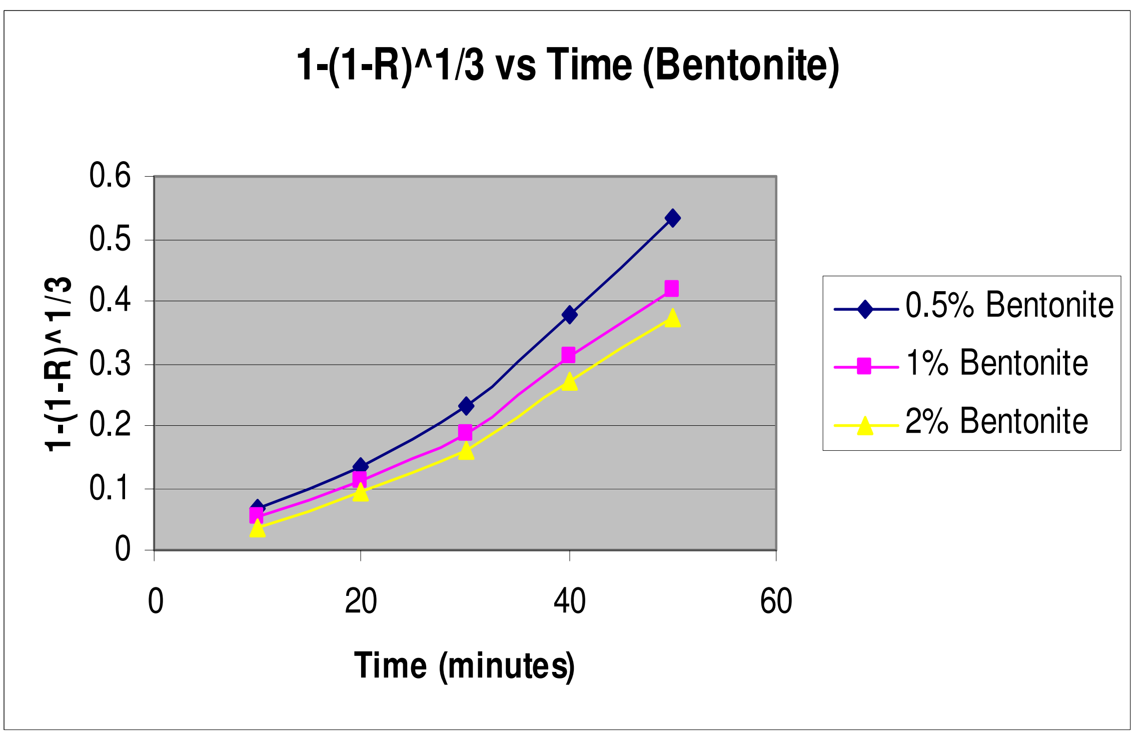


Table No. 6: $1-(1-R)^{1/3}$ versus Time for Pellets with Bentonite

Time (in minutes)	0.5% bentonite	1% bentonite	2% bentonite
10	0.0663	0.0538	0.0377
20	0.1355	0.1104	0.0918
30	0.2292	0.1857	0.1622
40	0.3786	0.3125	0.2247
50	0.5312	0.4191	0.3291

Figure No 8: $1-(1-R)^{1/3}$ versus Time for Pellets with Bentonite



Mechanism

The mechanism of reduction of iron ore (lump and pellets) occurs by three methods:

1. Chemical kinetics,
2. Diffusion control and
3. Mixed control (both chemical and diffusion process.)

With the help of the Arrhenius equation we can calculate the activation energy

$$\mathbf{K = A\ e^{-E/RT}}$$

Where,

K = Rate Constant, A= Arrehenius Constant, E= Activation Energy,

R= Gas Constant, T= Temperature.

When a graph is plotted between lnA and 1/T we get a straight line where,

x= (1/T), c=lnA

<u>ln(K) vs. (1/Tx10^4):</u>

We plotted the graph of ln (K) vs. (1/Tx10^4) for pellets with binder, with bentonite and with dextrin. Then calculated the value of Activation Energy from, $\mathbf{K = A\ e^{-E/RT}}$

Table No 7: ln K vs 1/T x 10^4 for 0.5 %Bentonite

Temperature (°C)	Temperature (K)	1/T x 10^4	K	ln K
900	1173	8.53	0.00359	-5.62
950	1223	8.18	0.00362	-5.34
1000	1000	7.86	0.00364	-5.04
1050	1323	7.559	0.0062	-5.09
1100	1373	7.283	0.0075	-4.89

Figure No 9: ln K vs 1/T x 10^4 for 0.5% Bentonite

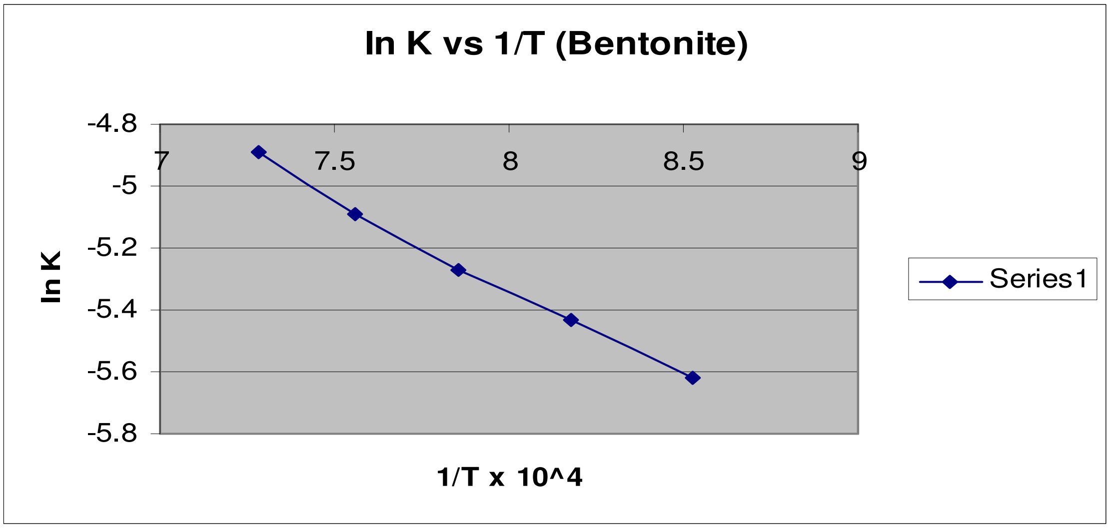
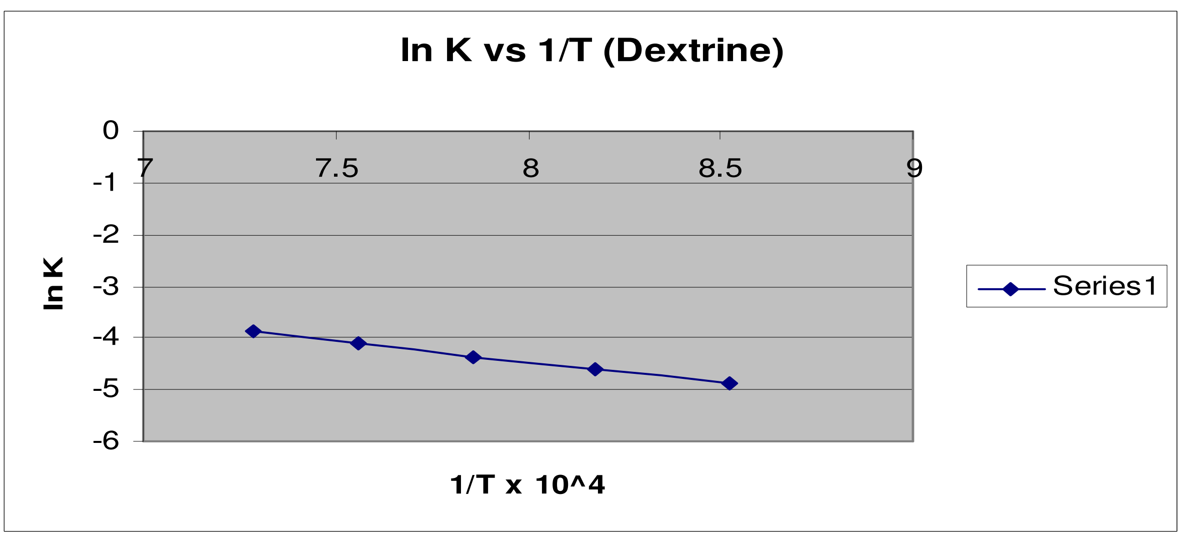


Table No 8: ln K vs 1/T x 10^4 for 0.5% Dextrine

Temperature (°C)	Temperature (K)	1/T x 10^4	K	ln K
900	1173	8.525	.0077	-4.87
950	1223	8.177	.0099	-4.62
1000	1273	7.855	.0128	-4.36
1050	1323	7.559	.0164	-4.11
1100	1373	7.283	.020	-3.89

Figure No 10: ln K vs 1/T x 10^4 for 0.5% Dextrine



RESULTS AND DISCUSSIONS

1. With Increase in temperature for a pellet the percentage reduction increases with the increase in time.
2. The percentage reduction in case of pellet with Dextrin was found more. This may be because of the lower activation energy of the pellets with dextrin as a binder.
3. A number of Models were considered out of which the model $1-(1-R)^{1/3}=kT$ exactly fits to our experimental values.
4. Activation Energy E was found to be 17.423 kcal/°C/mole for 0.5 % dextrine & 20.701 kcal/°C/mole for 0.5% Bentonite. Slope of this graph x (universal gas constant) = activation energy (E)
5. **So** the rate of reaction in case of pellets with Dextrin is faster than the rate of reaction of pellets with Bentonite.

CONCLUSION

- With increase in temperature, % reduction of pellets increases .
- With increase in time, % reduction of pellets increases
- Lower the binder percentage, greater the reducibility (.5% >1%>2%) of pellets
- Reduction of pellets with Dextrine binder is faster as compared to Bentonite
- Iron ore reduction kinetics follow Topochemical reaction nature
- Reduction reaction is temperature dependant.

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